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IR and NMR studies on zirconocene dichloride/methylalumoxane systems—catalysts for olefin polymerization

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Abstract

The interaction of zirconocene dichloride derivatives with methylalumoxane (MAO) was studied in toluene medium under argon and ethylene atmospheres by IR, ^{1}H, ^{13}C, ^{27}Al and ^{29}Si NMR spectroscopy. Data relating to polymerization of ethylene on these catalysts are given.

Introduction

Complexes of zirconocene compounds with methylalumoxanes (MAO) are known to possess a unique ability to catalyse olefin polymerizations [1–3]. Some more detailed studies of these soluble, extremely active catalytic complexes have been published. The effect of the nature of the alkylcyclopentadienyl ligands and of the structure of methylalumoxane upon polymer yield have been considered [4–7]. In order to find out the nature of the active sites these soluble catalytic systems have been studied by various spectral techniques [8–10]. The present paper deals with IR and NMR investigations of the catalytic complexes based on $(C_5H_4R)_2ZrCl_2$ (R = H, t-Bu, Me_3Si) and MAO.

Experimental

Zirconocene dichloride Cp_2ZrCl_2 was prepared from $ZrCl_4$ and CpMgCl by a standard method [11]. Zirconocene compounds $(C_5H_4R)_2ZrCl_2$ (R = t-Bu, Me_3Si)

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were prepared from $ZrCl_4$ and C_5H_4RLi in hexane–THF and recrystallized from toluene–hexane.

MAO was obtained from the direct hydrolysis of $AlMe_3$ (TMA) in hydrocarbons [12–13]. The dosage rate of H_2O was 0.066 mole/h. A MAO with molecular weight of 400 to 2300 was obtained depending on the molar ratio between TMA and H_2O. For the MAO with molecular weight 2300, the quantity of Me groups is 54.19%, and the quantity of the organically bonded Al is 39.20%.

The compounds decompose in air, so all manipulations were carried out in a Schlenk apparatus under argon atmosphere. The solvents were boiled over sodium and distilled off under argon atmosphere before use.

The IR spectra of samples were obtained with a Specord M-80 instrument as either KBr or CsI pellets prepared in a desiccator. NMR spectra were recorded on the following instruments: Bruker MSL-300 (300 MHz, ^1H) and Bruker AM-360 (93 MHz, ^1H and 360 MHz, ^{27}Al). The ^{13}C NMR spectra were recorded in the broad-band decoupling mode from the interaction of carbon nuclei with protons. As a reference signal for assignment of chemical shifts the NMR signals of such solvents as benzene and toluene have been used.

Polymerization was carried out in a 100 ml stainless steel reactor equipped with a stirrer and a sheath, in toluene solution (40 ml) at 70 °C for 20 minutes under constant ethylene pressure (7 atm). Zirconocene dichlorides and MAO were introduced to the reactor under argon as toluene solutions of known concentrations and after stirring for 20 minutes at 20 °C ethylene was added. The reaction was quenched with a 5% solution of HCl in isopropanol. The polymer was washed out with isopropanol and dried in vacuum at 80 °C to constant weight. The error in determination of polymer quantity was 5%.

Results and discussion

IR spectra

Interpretation of the vibrational spectra usually involves bond by bond consideration of the complexes. Within complexes $(C_5H_4R)_2ZrCl_2$ ($R = H$, t-Bu, Me_3Si) with MAO the following main bonds can be identified: C_5H_4R ligand, Zr–Cl, Al–O, Al–C. Variation in spectral characteristics of these bonds permits one to identify the nature of the complexation between the components of the catalytic system. The IR spectra of initial zirconocene derivatives show the absorption bands corresponding to η^5-C_5H_4R ligands, viz., 3100 cm^{-1} (C–H stretching), 1495 cm^{-1} (C–C stretching), 1000 cm^{-1} (C–H bending in plane) and 820 cm^{-1} (C–H bending out of plane) [14]. On complexation with MAO, the absorption bands of C_5H_4R ligands are actually unaffected, hence the character of the zirconium bond with the C_5H_4R ligand is maintained. Considerable variations in IR spectra characterise the absorption bands assigned to Al–O and Al–C bonds (Fig. 1). Compared with the initial MAO spectra, the intensity of lines increases dramatically and splitting of the bands for Al–O and Al–C bonds (600–850 cm^{-1}) occurs. This does not exclude structures like Zr–O–Al and Zr–Cl–Al–C from these complexes. In addition to the spectra of complexes some new bands at 1710 and 1785 cm^{-1} appear which are not observed for the initial compounds. These bands disappear rapidly when samples come into contact with air. The bands are not exhibited in the IR spectra of complexes formed in the presence of ethylene. Following earlier studies [15] we

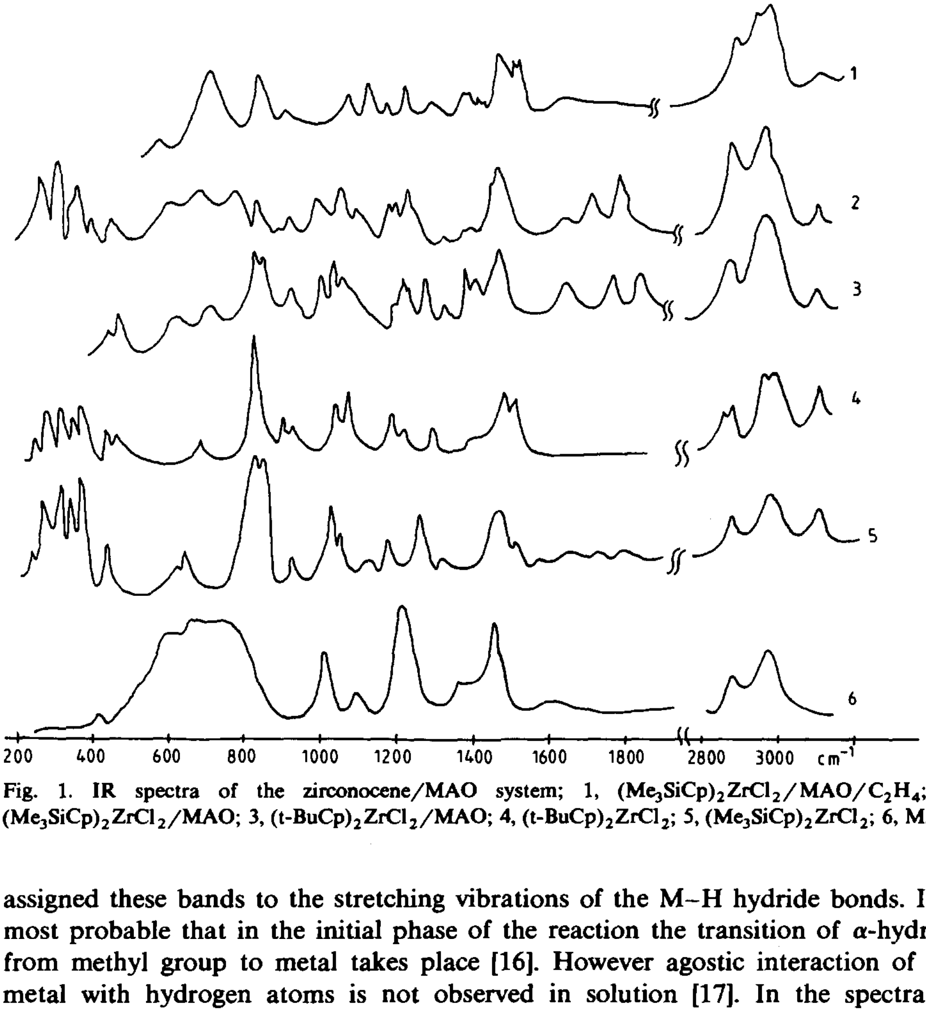

Fig. 1. IR spectra of the zirconocene/MAO system; 1, $(Me_3SiCp)_2ZrCl_2/MAO/C_2H_4$; 2, $(Me_3SiCp)_2ZrCl_2/MAO$; 3, $(t\text{-}BuCp)_2ZrCl_2/MAO$; 4, $(t\text{-}BuCp)_2ZrCl_2$; 5, $(Me_3SiCp)_2ZrCl_2$; 6, MAO.

assigned these bands to the stretching vibrations of the M–H hydride bonds. It is most probable that in the initial phase of the reaction the transition of α-hydride from methyl group to metal takes place [16]. However agostic interaction of the metal with hydrogen atoms is not observed in solution [17]. In the spectra of complexes formed in the presence of ethylene a new weak band appears at 1510 cm^{-1}, which can be assigned to stretching vibrations of the metal coordinated C=C double bond [18].

NMR study

The chemical shifts of the ^1H and ^{13}C nuclei in the zirconocenes that we used are listed in Tables 1 and 2. The incorporation of electron-donor groups into the cyclopentadienyl ring is known to cause strong deshielding of the carbon atom bonded with substituent (C1) while resonance is exhibited in a field that is weaker than that of the unsubstituted derivative [19]. At the same time C3,4 atoms are more effectively shielded than is the carbon atom in the unsubstituted ring. This kind of effect is peculiar to the tert-butyl substituent in $(C_5H_4Bu^t)_2ZrCl_2$ (Table 2). The trimethylsilyl group in the cyclopentadienyl ring initiates strong deshielding not only of the C1 nucleus, but also of the C2,5 nuclei due to the interaction of *d*-orbitals of the silicon atom with the π-system of the cyclopentadienyl ring. H2,5 protons of the ring containing Me_3Si substituent are subjected to strong deshielding.

Table 1

Chemical shifts (δ, ppm, C_7D_8) of the ^1H nuclei in the zirconocene/MAO systems

Complex	Protons of Cp ring	
	H2,5	H3,4
Cp_2ZrCl_2	5.90	5.90
Cp_2ZrCl_2/MAO	5.91; 5.78	5.91; 5.78
$Cp_2ZrCl_2/MAO/C_2H_4$	5.90	5.90
$(t\text{-}BuCp)_2ZrCl_2$	5.79	6.07
$(t\text{-}BuCp)_2ZrCl_2/MAO$	5.80; 5.38	6.08; 5.67
$(t\text{-}BuCp)_2ZrCl_2/MAO/C_2H_4$	5.80	6.10
$(Me_3SiCp)_2ZrCl_2$ [a]	6.43	5.99
$(Me_3SiCp)_2ZrCl_2/MAO$	6.40; 5.72	6.00; 5.30
$(Me_3SiCp)_2ZrCl_2/MAO/C_2H_4$	6.39; 5.72	5.97

[a] In C_6D_6.

On complexation of the zirconocenes with MAO in toluene and under ethylene atmosphere in this system some NMR signals in addition to those of the initial substances are observed (Tables 1, 2). In the Cp_2ZrCl_2/MAO system the signal for ^1H nuclei is shifted by 0.13 ppm and that for ^{13}C nuclei by 3.4 ppm towards the strong field. The addition of ethylene to this system reduces the difference between the initial complex and complexation product in chemical shifts (Table 3).

In the case of substituted zirconocenes, the differences between chemical shifts for H2,5 and H3,4 protons are shown to be similar. Here they are much greater than in unsubstituted zirconocene, and for systems $(t\text{-}BuC_5H_4)_2ZrCl_2/MAO$ and $(Me_3SiC_5H_4)_2ZrCl_2/MAO$ are 0.4 and 0.7 ppm respectively.

On complexation of $(t\text{-}BuC_5H_4)_2ZrCl_2$ with MAO the C2,5 and C3,4 nuclei in the cyclopentadienyl ring differ in degree of deshielding. It should be noted that a larger complexation effect is exhibited in the chemical shifts of the C3,4 nuclei. Table 3 shows that the addition of ethylene to the system results in more shielding of the C3,4 nuclei compared to the initial $(t\text{-}BuC_5H_4)_2ZrCl_2$ complex.

Table 2

Chemical shifts (δ, ppm, C_7D_8) of ^{13}C nuclei for zirconocene/MAO systems

Complex	Carbon atoms of Cp ring		
	C1	C2,5	C3,4
Cp_2ZrCl_2	116.6	116.6	116.6
Cp_2ZrCl_2/MAO	116.6; 113.4	116.6; 113.4	116.6; 113.4
$Cp_2ZrCl_2/MAO/C_2H_4$	116.6; 115.0	116.6; 115.0	116.6; 115.0
$(t\text{-}BuCp)_2ZrCl_2$	145.0	116.7	112.5
$(t\text{-}BuCp)_2ZrCl_2/MAO$	145.0; 146.0	116.9; 114.5	112.5; 108.5
$(t\text{-}BuCp)_2ZrCl_2/MAO/C_2H_4$	144.0	116.9	118.5
$(Me_3SiCp)_2ZrCl_2$	[a]	[a]	116.5
$(Me_3SiCp)_2ZrCl_2$ [b]	126.3	126.0	115.5
$(Me_3SiCp)_2ZrCl_2/MAO$	127.0	126.9; 124.0	116.2; 113.0
$(Me_3SiCp)_2ZrCl_2/MAO/C_2H_4$	126.5	126.3	116.0

[a] Signals masked by toluene. [b] In C_6D_6.

Table 3

Δ ^{13}C values (ppm) from initial zirconocenes for the substituted zirconocene dichlorides/MAO systems

Complex	C1	C2,5	C3,4
Cp_2ZrCl_2/MAO	3.2	3.2	3.2
Cp_2ZrCl_2/MAO/C_2H_4	1.6	1.6	1.6
(t-BuCp)$_2$ZrCl$_2$/MAO	−1.0	2.2	4.0
(t-BuCp)$_2$ZrCl$_2$/MAO/C_2H_4	1.0	−0.2	−6.0
($Me_3SiCp)_2ZrCl_2$/MAO	−0.7	2.0	3.5
($Me_3SiCp)_2ZrCl_2$/MAO/C_2H_4	−0.2	−0.3	0.5

On the other hand, the experiment shows that when $(Me_3SiC_5H_4)_2ZrCl_2$ undergoes what is assumed to be complexation with MAO and in the $(Me_3SiC_5H_4)_2$ $ZrCl_2$/MAO/ethylene system only slight changes in chemical shifts are observed. This can be explained in terms of the slight shielding of the ^{13}C nuclei in the cyclopentadienyl ring as compared to the initial $(Me_3SiC_5H_4)_2ZrCl_2$ complex. The small variation in chemical shifts for the ^{13}C nuclei of the ring is probably due to the interaction of the *d*-orbitals of the silicon atom with π-system of the Cp-ring prevailing over the complexation effect. These data agree with the result for ^{29}Si NMR. Chemical shifts of the ^{29}Si nuclei in $(Me_3SiC_5H_4)_2ZrCl_2$ are not affected by interaction with MAO nor by interaction with MAO and ethylene (4.09 ppm).

We have also studied the effect of ratio of the initial components upon complexation in Cp_2ZrCl_2/MAO/hexene-1 system. With a Cp_2ZrCl_2/MAO ratio of 1 : 5 in the ^1H NMR spectrum in the range of cyclopentadienyl protons, two singlets at 5.90 and 5.75 ppm with intensity ratios 1 : 0.44 (Fig. 2) are observed. The first signal corresponds to the protons of cyclopentadienyl ring pertaining to the initial Cp_2ZrCl_2 compound. We suggest that the second signal is initiated by protons of the cyclopentadienyl ligand of the zirconocene alkylated derivative. Previous data [20–22] suggest that this initial alkylation reaction takes place.

When hexene-1 is added to the reaction system (Cp_2ZrCl_2/MAO/hexene-1 = 1 : 5 : 1), the amount of Cp_2ZrCl_2 is decreased, while the intensity of protons of the methylated zirconium derivative is increased, the intensity ratios being 1 : 2.64. When MAO is increased (Cp_2ZrCl_2/MAO/hexane-1 = 1 : 10 : 1) the signal at 5.75 ppm is to be regarded as the main one.

On complexation of the substituted zirconocenes with MAO slight shifts of the methyl MAO groups towards the strong field of signals relating ^1H (0.01–0.02 ppm) and ^{13}C (3–4 ppm) are observed, which might indicate a decrease in the positive charge on aluminium atoms.

In the ^{27}Al NMR spectra of the Cp_2ZrCl_2/MAO and Cp_2ZrCl_2/MAO/hexene-1 reaction systems no essential changes as compared to the spectra for initial MAO are observed (Fig. 3). The ratio of ^{27}Al signals for 4- and 5-coordinated aluminium [23] is in fact maintained. However we do observe some changes which may be related to the 4-coordinated aluminium, and possibly indicative of varying the symmetry of the MAO molecules, and this is indirect evidence for its participation in coordination of the zirconium atoms. Analogous regularities in ^{27}Al NMR spectra for the systems $(Me_3SiC_5H_4)_2ZrCl_2$/MAO and $(Me_3SiC_5H_4)_2ZrCl_2$/MAO/ethylene have been observed.

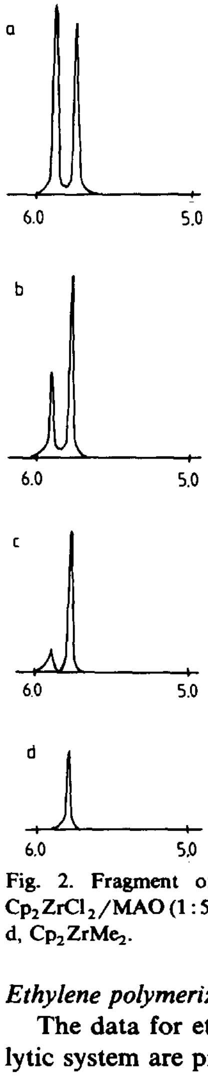

Fig. 2. Fragment of ^1H NMR spectra of zirconocene/MAO/hexene-1 system (δ, C_7D_8); a, Cp_2ZrCl_2/MAO (1 : 5); b, Cp_2ZrCl_2/MAO/hexene-1 (1 : 5 : 1); c, Cp_2ZrCl_2/MAO/hexene-1 (1 : 10 : 1); d, Cp_2ZrMe_2.

Ethylene polymerization

The data for ethylene polymerization on the zirconocene dichloride/MAO catalytic system are presented in Table 4. When $(Me_3SiC_5H_4)_2ZrCl_2$ is used instead of $(t\text{-}BuC_5H_4)_2ZrCl_2$ one observes the increase in the catalytic polymerization of ethylene. Increased activity of the $Cp_2Zr(CH_2SiMe_3)_2$ silicon derivative has been reported [10]. The review, ref. 24, describes many examples where the Me_3Si group affects the stereochemistry of organic reactions. Addition of organosilicon compounds to the titanium–magnesium catalysts improves their stereospecifity [25,26]. This effect is also exhibited when the silicon compound is used as an outer donor to complex with an organoaluminium compound and titanium [27]. When the silicon compound is the inner donor in a catalytic system [28], an increase in catalytic activity for olefin polymerizations is observed without improving stereospecifity. Some data, mainly relating to patents [29–31] are available for applying the transition metal/MAO system to silica.

It is also known that slight structural changes in bis(indenyl)zirconium complexes with dimethylsilyl bridges result in dramatic changes both in catalytic activity and in selectivity during olefin polymerizations [32].

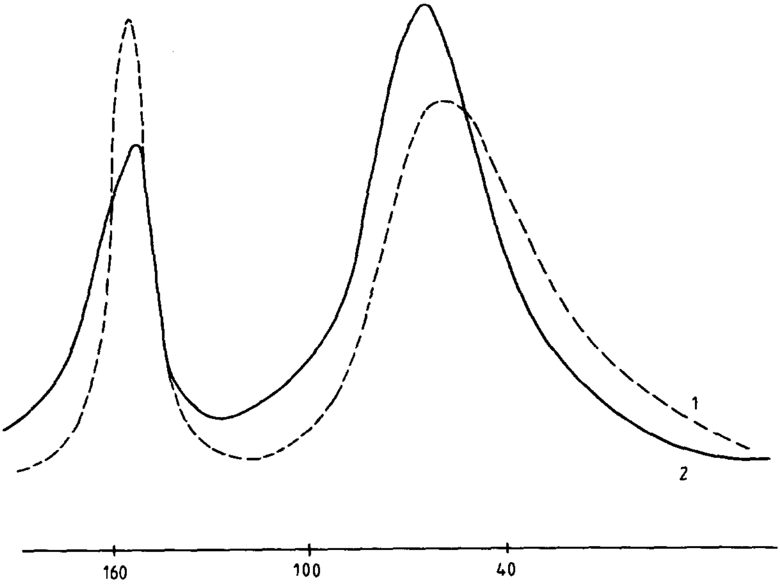

Fig. 3. ^{27}Al NMR spectra of 1, Cp_2ZrCl_2/MAO, and 2, MAO.

In our case, the somewhat higher activity of the system containing $(Me_3SiC_5H_4)_2ZrCl_2$ can be explained by various electron effects of the t-Bu and Me_3Si groups, as their steric effect should be similar. Quantum-chemical study of reactivity for the metal–carbon σ-bond has implied [33] that donor ligands decrease the tendency of transition metal to rearrange the electron structure, which determines the course of intrasphere concerted reactions. This is believed to reduce the reactivity of M–C bond, lowering the catalytic activity for olefin polymerization processes. Though this assumption agrees with our data it contradicts other conclusions [4] according to which the polymerization rates for olefins and the molecular weights of polymers in ethylene polymerization with a zirconocene catalyst, increase as the electron-donor effect of the alkyl substituent in the cyclopentadienyl ring is increased.

As observed from the ^{13}C NMR spectra, alkyl groups increase the electron density on the metallocene system [34]. However it was shown for toluene, that such redistribution is not due to the integrated charge transfer from the substituent (0.019 electron only), but occurs owing to the π-system polarization [35]. The role of the π-inductive effect was mentioned in a ^{13}C NMR investigation of ferrocene

Table 4

Ethylene polymerization activities for zirconocene/MAO catalysts

Zirconocene	$[Zr]\times10^6$ mole/l	[MAO] mole/l	Al/Zr	Yield	
				g	kg/mole × h
Cp_2ZrCl_2	3.4	0.038	11176	1.34	31500
$(t\text{-}BuCp)_2ZrCl_2$	3.4	0.038	11111	1.29	29900
$(Me_3SiCp)_2ZrCl_2$	3.2	0.038	11184	1.55	38100

derivatives [36]. At the same time, the difference in relative electron effect of alkyl groups is rather small and therefore it is difficult to postulate that the principal role in polymerization process is played only by the electron effect of substituents in the Cp rings of zirconocenes, considering the complexity of catalytic systems as a whole.

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